



Detection of gasoline on arson suspects' hands

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ABSTRACT

An arson suspect's contact with an ignitable liquid container can leave small traces of the substance on his hands, but detecting these traces is difficult. This research paper presents a method to obtain clear gasoline detection even 3 h after hands have been moistened with 50 μ L of gasoline using activated charcoal strips to adsorb the ignitable liquid traces directly from the suspect's hands. Light heating of the hands to 45 °C significantly increases the ability to detect gasoline traces.

This methodology is part of a system to sample a suspect's hands at the scene of crime or in a police station. Samples are taken by investigators then analyzed in a laboratory.

The suggested method provides an important improvement in detection sensitivity for ignitable liquids on suspect's hands.

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1. Introduction

Arson is one of the easiest crimes to commit. Even the use of a small amount of an ignitable liquid can cause considerable monetary damage as well as endanger human lives.

Ignitable liquids are used in a wide variety of activities in our daily lives. Gasoline is particularly common as a source of energy in vehicles. In Israel gasoline accounts for some 80% of the found flammable liquids in arson cases which are detected.

The process of arson is not at all complicated. A flammable liquid is poured on an item, and then ignited with a match. There is no need for professional knowledge, prior experience, or a license to possess a controlled substance. In the United States, for example, an estimated 30,500 cases of intentionally set fires in structures were reported by the U.S Fire Administration in 2008 alone. These fires took the lives of 350 persons [1].

The combustion process and associated heat release combine to create damage that reduces traces such as fingerprints and DNA [2], thus there is limited possibility to tie the perpetrator to the scene.

One forensic method to connect the perpetrator to the crime is to find evidence on his body. Contact with ignitable liquid when transporting it to the scene of crime, and particularly when pouring it, is apt to leave traces on clothes, shoes, or hands.

Previous studies have been conducted concerning the transfer and presence of ignitable liquids on clothes and shoes [3–5], but

very few studies have been published dealing with the detection of accelerants on the skin, and especially on the hands of a suspect.

There has been research concerning the penetration and adsorption of petroleum products into the skin. The basic working assumption is that hydrocarbons tend to remain in the outer skin layers, particularly in the stratum corneum [6,7].

Usual swabbing methods do not yield satisfactory results to extract ignitable liquids from hands, perhaps because hydrocarbon residues are trapped in the epidermis, and swab methods are not adequate to extract them [8,9].

A field test to readily sample and extract organic ignitable liquids on the palm of a suspect is required.

Almiral et al. propose an extracting method using solid phase microextraction (SPME) and further gas chromatograph (GC) analysis for traces of ignitable liquids on skin [10]. The method is sensitive, and a small amount of accelerant can be detected. Traces of ignitable liquids have been observed on hands more than 3 h after the application of 10 μ L of the substances. The method, however, is not very practical: the SPME fiber is not a field kit, and the suspect must be brought to a laboratory immediately after his arrest.

Darrer et al. suggest dressing the suspect's hands with polyvinyl, polyethylene or latex gloves for 20 min, then adsorbing the ignitable liquid residue on the gloves using an activated carbon strip (ACS) for 16 h at 60 °C. The ACS is then analyzed using gas chromatograph–mass spectrometer (GC–MS) [8]. In the article of Darrer et al. traces of gasoline are detected on gloves after several hours, when 500–1000 μ L of gasoline had been poured on the hand.

Montani et al. recently evaluated the amounts of different glove backgrounds; they suggest covering the suspect's hands with latex gloves. They even developed a prototype kit containing latex

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gloves for the sampling of ignitable liquids [9]. They mention that a decrease in the amount of gasoline is to be expected, but the timeframe is not clear. They do not relate to this decrease in an experimental mode.

This article proposes a new field test that is both practical and sensitive for extracting and sampling gasoline residues on the skin. A charcoal strip is placed on the suspect's palms, and the hand is inserted into a sealed bag at room temperature or with a gentle warming of the hand. The gasoline is extracted from the strip by dichloromethane (DCM) then examined by GC–MS.

Adsorption of vapors from ignitable liquid residues on charcoal strips is one of the most commonly used method for sampling fire debris prior to analysis, but there is no research into adsorption of ignitable liquids from hands by charcoal strips, probably because the technique usually requires heating of the exhibit for several hours [11–13].

In the research presented here the presence of a very little amount of gasoline was detected on the palm by adsorption with charcoal strips. Gasoline was used, because it is the most commonly encountered accelerant in Israel and probably throughout the world.

2. Materials and methods

2.1. Materials

- Lead-free gasoline of 95 octane was obtained from Paz Oils and Chemicals (Haifa, Israel).
- Dichloromethane (DCM) and N,N-dimethyl-formamide (DMF) AR were purchased from Bio Lab Ltd. (Jerusalem, Israel).
- M & Q polyamide roasting bags were purchased from Hanamal Packaging and Marketing Ltd. (Beer Yaakov, Israel).
- Nylon arson evidence bags were purchased from Grand River Products, LLC (Grosse Pointe Farms, MI).
- Activated charcoal strip devices (8 mm × 20 mm) were purchased from Albrayco Technologies, Inc. (Cromwell, CT).

2.2. Sampling procedures

Three volunteers participated to the experiment. Care was taken to prevent contamination:

- The strips were stored in closed nylon bags not kept in the laboratory.
- Hands were sampled before dripping the gasoline.
- The volunteers had no contact with ignitable liquids during the experiments.

Standard sampling was conducted for comparison: 1 μ L of gasoline was dripped on tissue paper and inserted into a nylon bag with half of an absorbent strip. The bag was heated for 15 h at 60 °C. Extraction from the strip was then performed using DCM.

Passive adsorption on charcoal strips at room temperature: 50 μ L of gasoline was dripped onto the palms of each of the three volunteers using a glass syringe. After 60 or 180 min half of a strip (8 mm × 10 mm) was placed on the palm, and the palm was sealed in a polyamide bag for 15, 60, 120 or 180 min.

Only half of the strip was used in all of the experiments, because the second half is used in the proposed method for blank processes.

Passive adsorption on charcoal strips with light heating: 50 μ L of gasoline was dripped by a glass syringe onto the palms of each of the three volunteers. After 60 or 180 min half of a strip (8 mm × 10 mm) was placed on the palm. The hand was then sealed in a polyamide bag heated at 45–48 °C by placement under a heating light (Phillips, 250 W) at a distance of 26 cm from the lamp for 15, 30 or 60 min.

2.3. Extraction from the strips and sampling to GC–MS

After the gasoline was adsorbed from the hand, the half strip was inserted into a conical vial, and 100 μ L of DCM was added for extraction of the gasoline.

The vials were vigorously agitated for 1 min, and then 5 μ L of the solvent was inserted into the injector of the GC–MS.

The analysis instrument was a Thermo Trace Ultra GC coupled with a Thermo DSQ quadrupole detector. The GC column was an Altech-fused silica capillary column 30 mm × 0.25 mm (i.d.) coated with AT-1 (0.25 μ m film). The column temperature was kept at 40 °C for 2 min, and then heated to 130 °C at a rate of 10 °C/min. The transfer line was kept at 250 °C, and the source temperature at 200 °C; the scan range was 30–300 Da; filament delay was 2 min. Carrier gas was helium; the flow was 3.2 mL/min. During the entire duration of the study maintenance tunes were performed daily to check the repeatability of the instrument. The injections were carried out in weak split mode, split ratio 3:1.

Integration was automatically done at ions 91, 105 and 119 by a qualitative identification processing setup of XCalibur (the Thermo instrument processing).

3. Results and discussion

Fig. 1 shows the total ion chromatography (TIC) adsorption at room temperature during 60 min. The beginning of the adsorption was 60 min after dripping 50 μ L of gasoline on the hand. Toluene, C₂-, C₃- and C₄-alkylbenzene are clearly seen. This chromatograph meets the ASTM requirements for the identification of gasoline [14].

The authors first examined the influence of adsorption time on the results. Adsorptions were performed at room temperature for different lengths of time. The strip was placed on the palm for 15, 60, 120 or 180 min, 1 h after dripping 50 μ L of gasoline.

After adsorption of 15 min the TIC chromatogram of gasoline was insufficient to conclude the presence of gasoline, however on

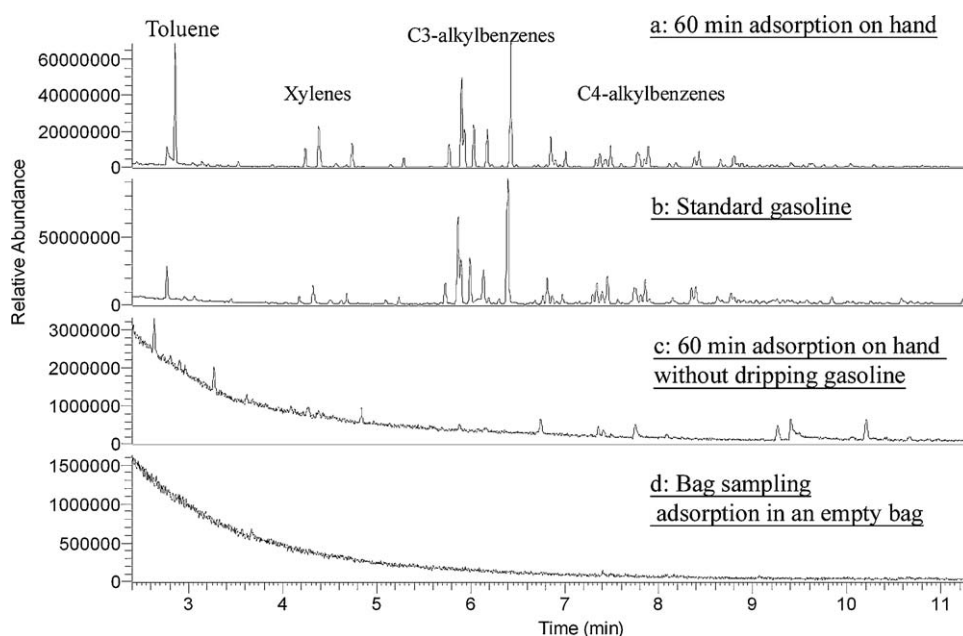


Fig. 1. TIC chromatograms (a) after adsorption during 60 min without heating. The beginning of the adsorption was 1 h after dripping 50 μ L of gasoline. (b) Standard gasoline. (c) Blank—60 min adsorption of hand without previous dripping of gasoline. (d) Blank—sampling by placing an ACS in an empty bag for 60 min.

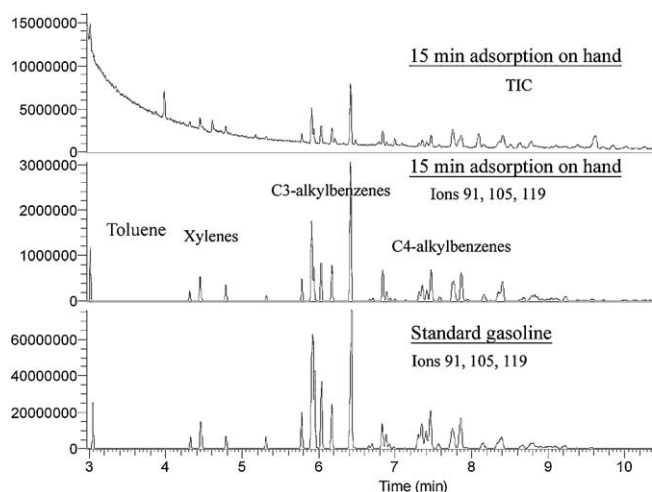


Fig. 2. TIC and extracted mass chromatogram (ions 91, 105 and 119) for adsorption during 15 min on hands. Below: extracted mass chromatogram of standard gasoline.

the extracted ion chromatogram (EIC) of 91, 105, 119 one can discern the profile of gasoline (see Fig. 2). The presence of these ions in the chromatogram enables one to focus on the typical mass spectra profile of gasoline and allows exclusion of foreign materials appearing in the TIC but not related to gasoline.

The profile of gasoline can be seen more clearly as the time of adsorption increases. After adsorption of 60 min or more, one can very clearly discern the typical aromatic hydrocarbons of gasoline: C₂-alkylbenzenes, C₃-alkylbenzenes and C₄-alkylbenzenes (see Fig. 3).

To improve and hasten adsorption the authors examined the influence of hand temperatures on the time of adsorption. Heat was applied by a heating lamp at 45 °C (it is also possible to use readily accessible items such as a hair dryer or a standard light bulb). The purpose of the heat is to increase perspiration and the evaporation of vapors of gasoline from the skin of the palm into the bag fastened around the hand. In parallel, the application of heat also increases the adsorption capability of the strip as described in other research reports [12,13].

It must be noted that the heating caused slight discomfort to the volunteers, but there was no damage. The person performing the

procedure must run the heating apparatus, taking care to avoid overheating and unnecessary pain to the suspect.

Fig. 4 shows three chromatograms of 15, 30 and 60 min of adsorption while applying light heat. It is possible to clearly discern the TIC profile of gasoline even after a short adsorption of 15 min. As in the previous experiment series, the beginning of adsorption was 1 h after moistening the hand with 50 µL of gasoline.

Integrations of specific ions 91, 105 and 119 were calculated to quantify results. This allows quantification of typical gasoline components while disregarding foreign materials not belonging to gasoline and appearing in the chromatograms. It is theoretically possible that foreign materials containing ions 91, 105 and 119 that do not belong to gasoline might be present on the hand, but the authors feel that this can be discounted.

Fig. 5 illustrates integration at various durations of adsorption at room temperature and with light heating. In all of the tests the beginning of the adsorption was 60 min after moistening the hand with 50 µL gasoline.

Standard deviations are calculated for every point in the figure. The relative high values of the standard deviations are a result of the differences between the volunteers.

Despite the fact that only a relatively small number of experiments was conducted, the basic conclusion is that there is a marked improvement in results as the exposure time to adsorbent material increases.

The rate of adsorption when lightly heating the hand significantly increases the amount of adsorbed gasoline.

The graph shows a significant improvement in the quantity of gasoline adsorbed when the hands are heated, as compared with adsorption without heating.

An experiment was undertaken to place an adsorbent strip on the hands with heating for 30 min, 3 h after moistening with gasoline. This simulated arrest of a suspect 3 h after purportedly committing an act of arson. Results were similar to adsorption during 15 min of heating done 60 min after moistening the hands with gasoline. As the time increases between moistening the hands with gasoline and the beginning of adsorption, a decrease in the amount of gasoline adsorbed is an anticipated result. The reason can be slow release of gasoline vapors trapped in the exterior layers skin, based upon physiological characteristics, body temperature, and/or the person's physical activity. It is possible to relate to the

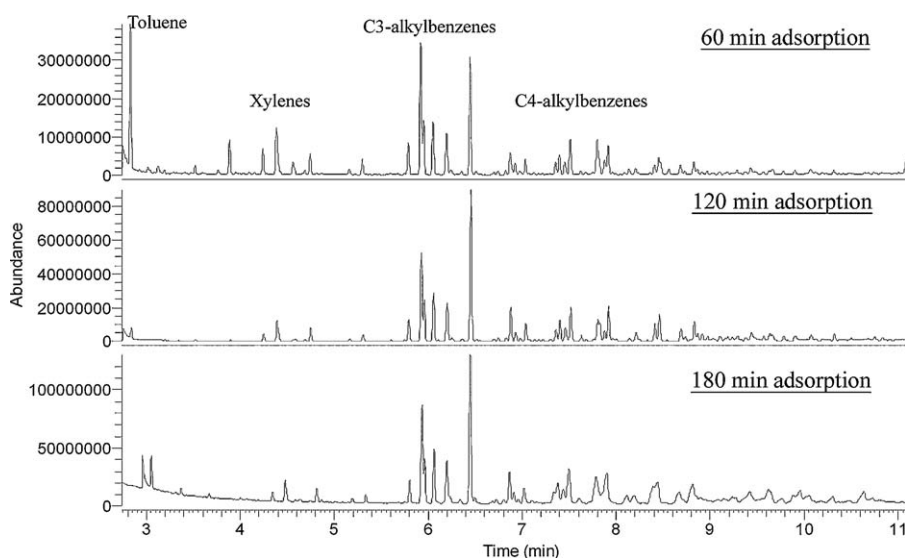


Fig. 3. TIC chromatograms of gasoline after adsorption of 60, 120 and 180 min. The beginning of the adsorption was 1 h after dripping.

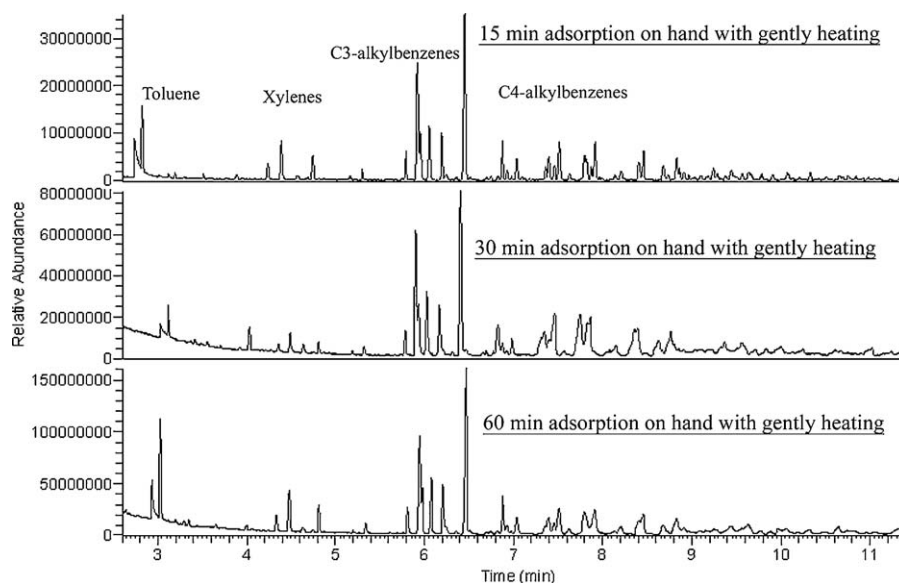


Fig. 4. TIC chromatograms after adsorption with slight warming for 15, 30 and 60 min. One hour after dripping 50 μ L of gasoline.

hand as one would relate to an adsorbent sponge, which releases flammable material as time passes. Washing of the hands is apt to cause a significant decrease in the amount of adsorbed gasoline. The implication of these findings is that the investigating unit must work quickly from the time of a suspect's arrest until sampling his hands.

Adsorption after moistening the back of the hand with 50 μ L of gasoline and placing the adsorbent material inside the palm for 60 min yields a less intense identification of the ignitable liquid, but still in accordance with ASTM protocol (Fig. 6).

It is the authors' recommendation always to place adsorbent material on the suspect's palm, even when it is probable that the back of the hand was moistened with gasoline, since it is highly probable that the palm is also wet.

In these experiments wrapping the hands with bags is preferred rather than wrapping them in gloves: It is the authors' estimation that gloves can create separate air pockets and reduce exposure to the adsorbent material. When the strip is on the palm inside a bag, it is exposed to gasoline vapors from the entire palm including part of the fingers.

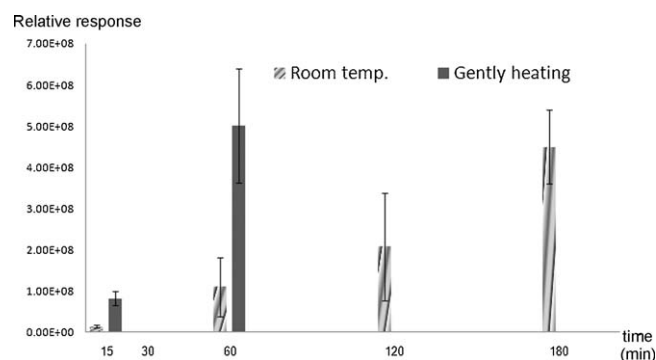


Fig. 5. Integration of the obtained relative responses of ions 91, 105 and 119. Adsorption was done 60 min after wetting the hand with 50 μ L of gasoline, with and without light heating. The timescale is the duration of adsorption.

A variety of gloves examined create "noise" from different types of plastics such as aromatic components, interfering with the gasoline chromatogram [9]. The polyamide bags used in this research project are virtually noise-free (Fig. 1).

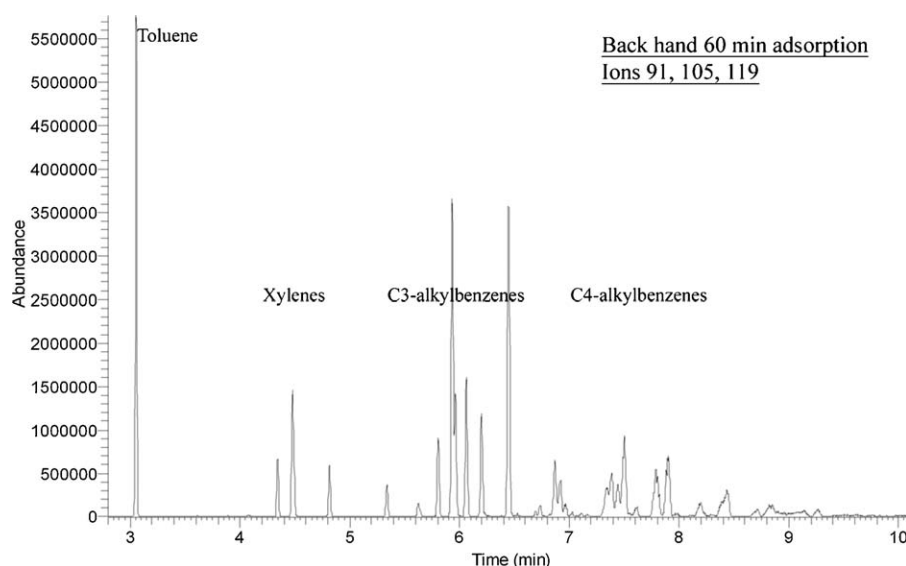


Fig. 6. EIC of ions 91, 105 and 119 obtained after dripping on the back of the hand and placing an adsorbent strip in the palm.

Given this background, the recommended work procedure is to place a half strip on the palm and wrap the hand in a sealed polyamide bag. The second half of the strip is used for a blank test. Before sampling suspects, one should establish an adsorption standard using the hand of a non-suspect who did not come in contact with an ignitable liquid this is to establish the threshold of sensitivity.

Use of this procedure on the hands of gasoline fuel attendants shows an extremely small quantity of gasoline, even less than the 50 μL used in the moistening test. This point again raises the importance of using a control blank to preclude contamination.

The recommended method is as follows:

A wrapped strip is opened a short time before the examination and after the suspect is detained. The strip is divided in half. One half is wrapped without being used and placed immediately into hermetically sealed bag (quality control); the second half is placed on the suspect's palm. This procedure is carried out on each of the suspect's hands. When possible it is recommended to warm the suspect's hands by hair dryer or a regular light bulb to a temperature of not more than 45 °C. Ideal adsorption time with light heating is between 15 and 30 min. If heating is not possible, recommended adsorption time is between 60 and 120 min. At the end of the procedure the second half of the strip should be placed into hermetically sealed bags. This means that the laboratory will receive four half strips labeled: "R" right hand, "RB" right hand blank, "L" left hand, "LB" left hand blank.

4. Conclusion

A new procedure is presented for the detection of gasoline on the hands of a suspect. The method describes a highly sensitive process for sampling a suspect's hands a short time after arson has been committed, then analysis in a laboratory. Even 3 h after a small quantity of gasoline comes into contact with hands, it has been possible to detect the presence of this ignitable liquid with the proposed procedure.

The research shows the effectiveness of the use of passive adsorption for a reasonable length of time on a suspect's palm. A significant increase in adsorbed ignitable liquid is obtained with heating at 45 °C. The purpose of the heating is to cause the hand to perspire and the gasoline to evaporate, with emphasis to avoid overheating and unnecessary pain to the suspect.

The described method must be followed carefully before it can be introduced as court evidence, and it should be stressed that a

quality assurance critique (no gasoline on the blanks) is required to prevent errors. This also means that the examiner must be absolutely certain that the source of ignitable liquid sample examined is from the suspect's hands and not elsewhere.

The method has been introduced on a trial basis in selected Israel Police Stations'. In two different cases gasoline was identified on suspects' hands a few hours after arsons were perpetrated.

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